

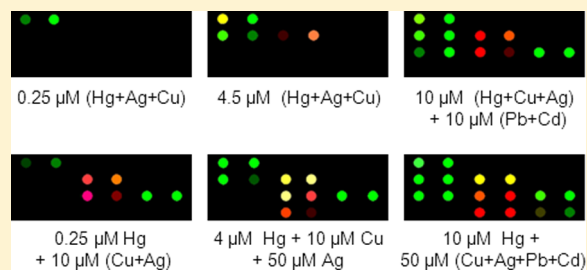
Paper-Based Colorimetric Array Test Strip for Selective and Semiquantitative Multi-Ion Analysis: Simultaneous Detection of Hg^{2+} , Ag^+ , and Cu^{2+}

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Supporting Information

ABSTRACT: A novel approach is presented in this article to qualitatively and semiquantitatively analyze multiple heavy metal ions simultaneously by a colorimetric array test strip. As a proof-of-concept application, a multi-ion analysis array test strip (for Hg^{2+} , Ag^+ , and Cu^{2+}) was fabricated through immobilizing five specifically responsive indicators in typical matrixes with tunable sensitivities. The as-obtained test strip shows not only high selectivity for Hg^{2+} , Ag^+ , and Cu^{2+} , respectively, but also can be applied for their mixtures. The detection limit of the test strip is well below the Chinese wastewater discharge standard concentrations. Moreover, the array test strip demonstrates excellent anti-interference capability, detection, and production reproducibility, long-term storage stability, and real water sample applicability.



With the rapid development of industries, heavy metals containing wastewaters are increasingly discharged into the environment in recent decades, especially in developing countries.¹ The heavy metals exist in wastewaters mainly as their cationic forms, and the metal ions will be accumulated millions of times by fish or shellfish even at very low concentrations. Because these heavy metal ions are not degradable in the environment, they are extremely harmful to human health, such as causing serious damage to the human's central nervous system, kidneys, livers, bones, and teeth, when they enter into the human food chain.² Therefore, the detection of heavy metal ions, particularly in aquatic ecosystems, is very important considering their severe effects to human health.

Numerous traditional techniques, mainly including inductively coupled plasma mass spectrometry (ICPMS) and atomic absorption/emission spectroscopy,^{3–6} are available for heavy metal ions detection; however, the range of their applications is highly limited by the high-cost and nonportability of these instruments, sophisticated sample preparation, and the need of professional operation. Therefore, it is still highly desired of the development of new simple, rapid, inexpensive, and on-site applicable detection methods for heavy metal ions.

In recent years, many efforts have been paid to develop optical chemosensors and biosensors to determine metal ions.^{7–12} These sensor-based methods mostly show superior selectivity and sensitivity, but usually require complicated design and synthesis steps. In addition, numerous metal ions generally coexist in analytical samples, and their simultaneous detection is more practically important. Fortunately, a variety of techniques have shown such capability.^{13–39} In these developed methods, electroanalytical,^{17–19} multichannel/multidimensional,^{20–23} and sensor array techniques^{24–39} attracted much

attention and had been applied successfully for detection and discrimination of multiple analytes. Particularly, Suslick's group obtained great achievements in application of the colorimetric sensor array technique for differentiating many chemical properties alike analytes in recent years, such as toxic industrial gases, volatile organic compounds, bacteria, and pathogenic fungi, etc.^{26,35–39} These techniques indeed effectively improved detection efficiency, but their limitations clearly existed as well. For example, relatively complicated design and fabrication processes are usually required and/or can hardly be applied for mixtures of analytical samples.

It is known that the sensing properties (sensitivity and selectivity) of an embedded indicator are significantly affected by immobilization matrixes,^{40–42} but unfortunately, these unique features did not yet receive enough attention. Moreover, the immobilization of a specifically responsive indicator into an appropriate porous matrix actually offers several advantages: (i) obtaining a tunable sensitivity; (ii) porous matrix serving as a preconcentrator and enriching the analyte and thus enhancing detection sensitivity; (iii) improving stability and solubility of indicators. Inspired by this knowledge, we proposed to fabricate a qualitative and semiquantitative multianalyte analysis test strip through embedding specifically responsive indicators into appropriate matrixes with expected sensitivities. It is worthy to note that the basic principle for design and fabrication of our colorimetric array test strip is different from that of Suslick's group. They commonly applied a variety of cross-reactive indicators to fabricate an array.^{35–39} This kind of design is

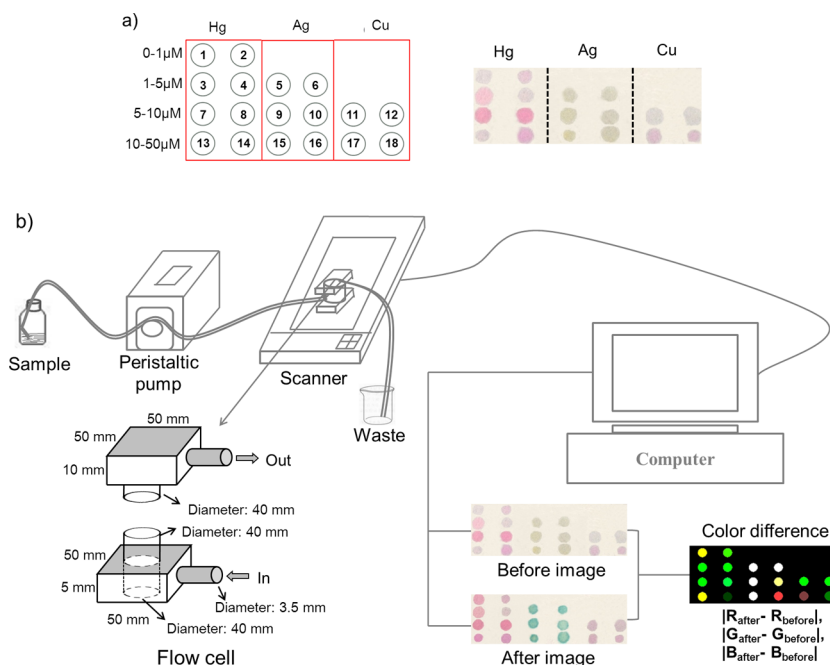


Figure 1. (a) Layout of the as-fabricated colorimetric array test strip (left) and its real image (right). (b) The experimental setup for sensing heavy metal ions with the developed colorimetric array test strip and a schematic illustration of data analysis.

beneficial in discrimination among chemical structures and/or properties alike analytes, but it can hardly recognize different components in a mixture sample.^{24–39} In contrast, we use specifically responsive indicators and tune their sensitivities by embedding them in appropriate matrixes. Such a design allows for simultaneous detection of multiple analytes (even in a mixture) in both qualitative and semiquantitative manners.

As a proof-of-concept application of the above design strategy, in this current study, five specifically responsive heavy metal ions indicators (for Hg^{2+} , Cu^{2+} , and Ag^{+}) were selected and their tunable sensitivities to the corresponding metal ions were accomplished through screening a large number of immobilization matrixes. Then, a paper-based colorimetric array test strip was subsequently fabricated by “printing” the indicator-containing formulations onto a solid substrate (filter paper here). The as-obtained test strip can be applied not only to selectively detect the individual metal ions of Hg^{2+} , Cu^{2+} , and Ag^{+} semiquantitatively, but their mixtures simultaneously, with sensitivities satisfying the Chinese wastewater discharge standard concentrations.⁴³ Moreover, this test strip shows excellent anti-interference capability against many other metal ions, real water samples applicability, and long-term storage stability. The described technique in this article may give a potentially simple, highly efficient, and inexpensive way for on-site monitoring heavy metal ions and might be expanded for other pollutants.

EXPERIMENTAL SECTION

Materials. Tetraethoxysilane (TEOS), methyl trimethoxysilane (MTMS), methyl triethoxysilane (MTES), poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (NPOE), dioctyl sebacate (DOS), and tri(2-ethylhexyl)phosphate (TEHP) were purchased from Aldrich chemical company. Indicator 5 and the starting materials for preparation of indicators 1–4 were obtained from Sinopharm Chemical Reagent. Metal salts (as their perchlorates) were acquired from J&K Scientific Ltd. All the chemicals were used directly without further purification

unless otherwise specified. Distilled water was used throughout the experiments. Real water samples were simply collected from our lab’s tap and the pond in our institute. Indicators 1–4 were characterized by 1H and ^{13}C NMR (400 MHz AVANCE III NMR spectrometer) and electrospray ionization mass spectrometry (ESI-MS) (JEOL JMS-T100LC mass spectrometer).

Synthesis and Characterization of the Indicators 1–4.

Indicator 1 was synthesized referring to the reported procedure.⁴⁴ 1H NMR ($CDCl_3$), δ (ppm): 1.17 (t, 12H, NCH_2CH_3), 3.33 (q, 8H, NCH_2CH_3), 3.61 (bs, 2H, NH_2), 6.28 (dd, 2H, xanthene-H), 6.41 (d, 2H, xanthene-H), 7.10 (dd, 1H, Ar-H), 7.42 (d, 2H, Ar-H), 7.93 (dd, 1H, Ar-H). ^{13}C NMR ($CDCl_3$), δ (ppm): 12.6, 44.4, 65.9, 98.0, 104.6, 108.1, 123.0, 123.8, 123.9, 128.1, 130.0, 132.5, 148.9, 151.5, 153.8, 166.1. ESI-MS [$(C_{28}H_{32}N_4O_2)(H)^+$]: calcd m/z = 457.3, found m/z = 457.3.

Synthesis of 2. Rhodamine B base (1.00 g, 2.26 mmol) and Lawesson reagent (0.92 g, 2.27 mmol) were dissolved and refluxed in 20 mL of absolute benzene for 4 h under N_2 atmosphere. After evaporating the solvent under reduced pressure, the residue was purified by flash chromatography with CH_2Cl_2 /petroleum = 1:1 as eluent to get a pale yellow solid. This solid (0.20 g, 0.44 mmol) was then dissolved in 20 mL of hot ethanol, followed by addition of ethylenediamine (134 μ L, 2.0 mmol). The mixture was refluxed for 4 h until the fluorescence of the solution was disappeared. The reaction was then cooled to room temperature and precipitate was collected and rinsed with 10 mL of cold ethanol. Crude product was purified by recrystallization from acetonitrile to give 60 mg of **2** (white solid) in 27% yield. 1H NMR ($CDCl_3$), δ (ppm): 1.19 (t, 12H, NCH_2CH_3), 2.03 (s, 2H, NH_2), 2.51 (t, 2H, NH_2-CH_2), 3.35 (q, 8H, NCH_2CH_3), 3.59 (t, 2H, $NH_2-CH_2-CH_2$), 6.27 (dd, 2H, xanthene-H), 6.37 (d, 2H, xanthene-H), 6.38 (d, 2H, xanthene-H), 7.12 (d, 1H, Ar-H), 7.50 (dt, 2H, Ar-H), 8.16 (d, 1H, Ar-H). ^{13}C NMR ($CDCl_3$), δ (ppm): 14.7, 29.7, 38.3, 46.2, 73.9, 96.7, 104.1, 118.4, 123.3, 125.1, 127.9, 128.6, 132.6, 137.9,

148.0, 151.0, 151.7, 191.7. ESI-MS $[(C_{30}H_{36}N_4OS)(H)]^+$: calcd $m/z = 501.3$, found $m/z = 501.3$.

Synthesis of 3. The intermediate product for **2** (0.50 g, 1.1 mmol) and Lawesson reagent (0.49 g, 1.2 mmol) were dissolved and refluxed in 20 mL of absolute benzene for 4 h under N_2 atmosphere. After the solvent was evaporated under reduced pressure, the residue was purified by silica gel column chromatography with CH_2Cl_2/n -hexane = 1:1 as the eluent to give **3** as a magenta solid in 21% yield (110 mg). 1H NMR ($CDCl_3$), δ (ppm): 1.19 (t, 12H, NCH_2CH_3), 3.35 (q, 8H, NCH_2CH_3), 6.32 (dd, 2H, xanthene-H), 6.36 (d, 2H, xanthene-H), 6.74 (d, 2H, xanthene-H), 7.19 (d, 1H, Ar-H), 7.49 (d, 1H, Ar-H), 7.57 (dt, 1H, Ar-H), 8.13 (d, 1H, Ar-H). ^{13}C NMR ($CDCl_3$), δ (ppm): 12.6, 44.4, 68.8, 97.8, 107.0, 108.4, 123.8, 126.9, 128.4, 129.7, 133.7, 142.5, 148.7, 152.3, 156.7, 227.6. ESI-MS $[(C_{28}H_{30}N_2OS_2)(H)]^+$: calcd $m/z = 475.2$, found $m/z = 475.2$.

Synthesis of 4. Compound **1** (0.23 g, 0.50 mmol) and excess 2,4-dihydroxy-benzaldehyde (2.0 mmol) were dissolved and refluxed in 20 mL of absolute ethanol for 6 h. After the solution was cooled and concentrated to 10 mL and allowed to stand at room temperature overnight. The precipitate which appeared next day was filtered and rinsed three times with 10 mL of cold ethanol. After drying under reduced pressure, the reaction afforded 0.18 g of **4** as a pink solid (63% yield). 1H NMR ($CDCl_3$), δ (ppm): 1.17 (t, 12H, NCH_2CH_3), 3.33 (q, 8H, NCH_2CH_3), 6.27 (dd, 2H, xanthene H), 6.32 (d, 2H, xanthene H), 6.48 (d, 2H, xanthene H), 6.99 (dd, 1H, Phen-H), 7.03 (d, 1H, Phen-H), 7.17 (dd, 1H, Phen-H), 7.19 (d, 1H, Ar-H), 7.53 (m, 2H, Ar-H), 7.98 (d, 1H, Ar-H), 9.22 (bs, 1H, $N=C-H$), 11.05 (bs, 2H, Phen-OH). ^{13}C NMR ($CDCl_3$), δ (ppm): 12.6, 44.3, 66.6, 98.1, 103.4, 105.5, 107.1, 108.1, 112.3, 123.2, 124.1, 128.1, 128.5, 130.2, 133.1, 133.2, 149.1, 150.6, 153.6, 154.0, 159.0, 160.6, 164.1. ESI-MS $[(C_{35}H_{36}N_4O_4)(H)]^+$: calcd $m/z = 577.3$, found $m/z = 577.3$.

Fabrication of Colorimetric Array Test Strip. Sol-gel (acid-catalyzed hydrolysis of solutions containing TEOS, MTMS, or MTES) or polymer (PVC mixed with a plasticizer of NPOE, DOS, or TEHP) formulations were generally used to immobilize indicators **1–5** (Supporting Information Table S2). After screening detection properties of indicators **1–5** in all these formulations to metal ions at various concentrations, tunable sensitivities of the embedded indicators **1–5** for their corresponding heavy metal ions (i.e., Hg^{2+} , Ag^+ , or Cu^{2+}) can be achieved by typical formulations (see Supporting Information Table S1 for details). The indicator-containing formulations (total 18) were then “printed” on a Whatman grade no. 1 quantitative filter paper (GE Healthcare, U.K.) with a layout as shown in Figure 1a. Once coated, the test strip was allowed to set in air for 0.5 h and then stored in a nitrogen-filled desiccator for 3 days before any experiments were performed.

Experimental Setup, Procedure, and Data Analysis. It is schematically illustrated in Figure 1b the experimental setup for detecting heavy metal ions with the developed colorimetric array test strip. A desired concentration of the heavy metal ion solution was pumped into a homemade poly-(tetrafluoroethylene) flow cell using a peristaltic pump (Baoding longer precision pump) through the filter paper from bottom to top.

For all sensing experiments, imaging the array test strip was taken using a flatbed scanner (Epson Perfection V300). The “before” image was obtained after 10 min of exposure to

deionized water. The after images were acquired after every minute of exposure to a heavy metal ion solution at a steady flow rate of 3.0 mL/min until 15 min. The difference maps were obtained by the following steps: (i) converting every printed spots in the “before” and “after” images into red, green, and blue (RGB) values using Adobe Photoshop software; (ii) subtracting RGB values of every printed spots in an “after” image from the corresponding “before” image; (iii) acquiring an image, i.e., a difference map, from the subtracted RGB values using Adobe Photoshop software. The color changes of the array can be quantitatively illustrated by the total Euclidean distances (EDs), which could be defined by the following formula:

$$ED = \sqrt{(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2}$$

According to the relationship between the color changes of the array test strip (i.e., EDs) and a sample solution exposure time, as shown in Supporting Information Figure S1, 10 min is generally required to reach a saturation response; therefore, 10 min of exposure is taken as the “after” image throughout this study.

RESULTS AND DISCUSSION

Design and Fabrication of the Colorimetric Array Test Strip. The traditional colorimetric sensor array technology generally uses nonspecific indicators, but the key point of our colorimetric array test strip is the use of a few specifically responsive indicators which are embedded in appropriate matrixes with tunable sensitivities. This design allows us to detect multiple analytes simultaneously in both qualitative and semiquantitative manners without complex statistical analysis process. As a proof-of-concept application, in this study, five specifically responsive indicators **1–5** (see Figure 2 for their

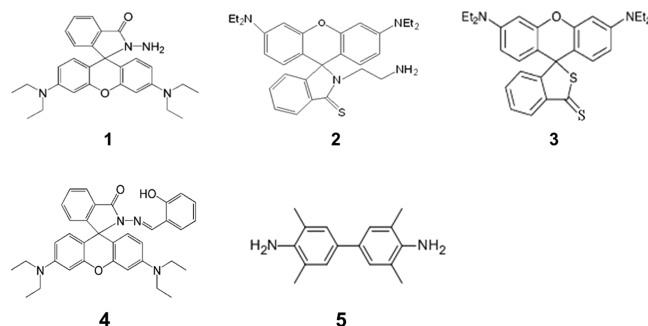


Figure 2. Chemical structures of five indicators used in this study, of which **1–3**, **4**, and **5** are designed to selectively respond to Hg^{2+} , Cu^{2+} , and Ag^+ , respectively.

chemical structures) to heavy metal ions Hg^{2+} , Ag^+ , and Cu^{2+} were selected and embedded in appropriate matrixes with tunable sensitivities using typical formulations (see the Supporting Information Table S1 for the details of the applied formulations). Due to the lack of a general guideline to tune sensitivity of an embedded indicator, careful screening tests have to be performed to find an appropriate formulation to immobilize an indicator with a typical sensitivity. In this current study, 20 formulations (listed in Supporting Information Table S2) were employed to immobilize the indicators **1–5**, and their responses to metal ions (Hg^{2+} , Cu^{2+} , Ag^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+}) at various concentrations were fully investigated. Then, those conditions

with desired sensitivities were picked and used to fabricate our array (total 18 as shown in Supporting Information Table S1). Finally, an array-type of colorimetric test strip was fabricated by “printing” the indicator-containing formulations onto a filter paper with a layout as shown in Figure 1a. Note that two spots are always used for a particular sensitivity of a heavy metal ion to ensure detection reliability.

Detection Performances of the Test Strip to Hg^{2+} , Ag^+ , and Cu^{2+} . To explore sensing performances of the developed colorimetric array test strip for Hg^{2+} , Ag^+ , and Cu^{2+} , their individuals and mixtures at various concentrations were widely examined. As shown in Figure 3, the colorimetric array

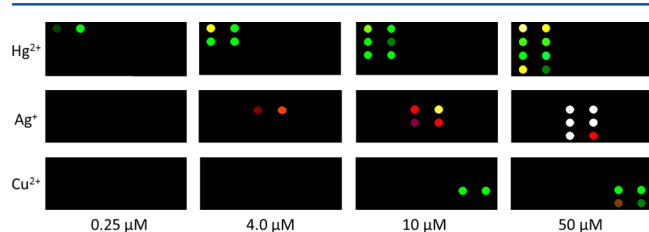


Figure 3. Typical responses of the developed array test strip to the individual Hg^{2+} , Ag^+ , and Cu^{2+} at 0.25, 4.0, 10, and 50 μM . For purposes of visualization, the color range of these difference maps was expanded from 2 to 8 bits per color (RGB range of 2–5 expanded to 0–255).

test strip displays different response patterns (ΔR , ΔG , ΔB) to each of the three heavy metal ions at various concentrations (i.e., 0.25, 4, 10, and 50 μM). A unique feature is found that the sensing spots are gradually lighting up from top to bottom with concentrations of a typical metal ion increasing. More interestingly, the responses of the test strip to mixtures of Hg^{2+} , Ag^+ , and Cu^{2+} show simply ensemble results from their individuals (Figure 4). These observations demonstrate that

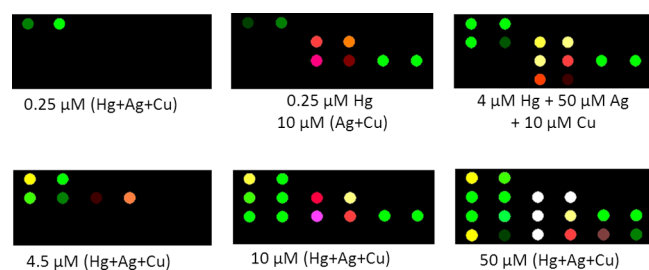


Figure 4. Typical responses of the developed array test strip to mixtures of Hg^{2+} , Ag^+ , and Cu^{2+} at different concentrations. For purposes of visualization, the color range of these difference maps was expanded from 2 to 8 bits per color (RGB range of 2–5 expanded to 0–255).

this developed colorimetric array test strip can be potentially employed for determining the three heavy metal ions (i.e., Hg^{2+} , Ag^+ , and Cu^{2+}) simultaneously in both qualitative and semiquantitative manners without cross-interference whatever they are in single or mixed forms. These results as well as indicate that through embedding specifically responsive indicators into appropriate matrixes is indeed an efficient way to tune their sensitivities and consequently for semiquantitative detection. The developed test strip herein permits fast, inexpensive, and highly efficient discrimination and identification of Hg^{2+} , Ag^+ , and Cu^{2+} simultaneously over a wide range of concentrations with sensitivities satisfying the Chinese

wastewater discharge standard concentrations (i.e., Hg , 0.25 μM ; Ag , 4.63 μM ; Cu , 15.74 μM).⁴³

Relationship between Test Strip Responses and Concentrations of Hg^{2+} , Ag^+ , and Cu^{2+} . To evaluate capabilities of the test strip for more accurate sensing, we next examined the relationship between the array’s responses (total EDs of the color changes, i.e., square root of the sums of the squares of the ΔRGB values) and the concentrations of the three heavy metal ions. Figure 5 showed the total EDs of the

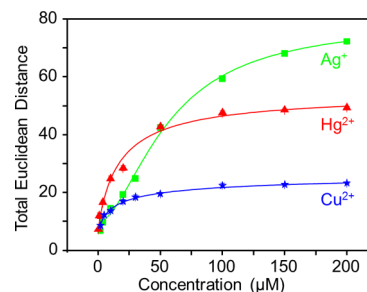


Figure 5. Total Euclidean distances of the array test strip plotted vs different concentrations of Hg^{2+} , Ag^+ , and Cu^{2+} . All of the experiments were run in triple, and the error bars shown are the standard deviation of triple trials.

array test strip plotted versus different concentrations of Hg^{2+} , Ag^+ , and Cu^{2+} , respectively. It is clearly to see that the EDs increased gradually with the concentrations of the three heavy metal ions increasing, and nice sigmoidal fitting curves can be obtained. Therefore, a more accurate semiquantitative analysis can be achieved based on these fitting curves.

Moreover, by means of extrapolating from the observed test strip response at the lowest investigated concentration, we can estimate the limit of detection (LOD) for each heavy metal ion. Herein, we define a conservative LOD for our test strip response as the heavy metal ions concentration need to give 3 times the signal-to-noise (S/N) versus background for the sum of the three largest responses color changes to Hg^{2+} , Ag^+ , and Cu^{2+} , respectively. The results of calculation revealed that the LODs for Hg^{2+} , Ag^+ , and Cu^{2+} were 0.19, 1.69, and 1.40 μM , respectively, all of which are lower than their Chinese wastewater discharge standard concentrations.⁴³

Stability and Reproducibility. To be a practical application of this colorimetric array test strip, its detection and production reproducibility and shelf-life stability should be considered as some of critical factors. First, Hg^{2+} , Ag^+ , and Cu^{2+} in quadruplicate trials at 50 μM were performed and highly analogous results were observed, and this demonstrates good detection reproducibility of the array test strip (Supporting Information Figure S2). Second, responses of three independent printing batches of test strips to Hg^{2+} , Ag^+ , and Cu^{2+} at 50 and 10 μM were examined, and the observed closely identical results indicate excellent production reproducibility (Supporting Information Figure S3). Finally, the storage shelf-life of the developed test strip was as well examined. As shown in Supporting Information Figure S4, insignificant changes of the test strip responses to the three heavy metal ions over a 4 week period were found when storing in a nitrogen-filled desiccator. These results demonstrate excellent detection and production reproducibility and long-term storage stability of the array test strip to Hg^{2+} , Ag^+ , and Cu^{2+} , revealing potentially practical applications.

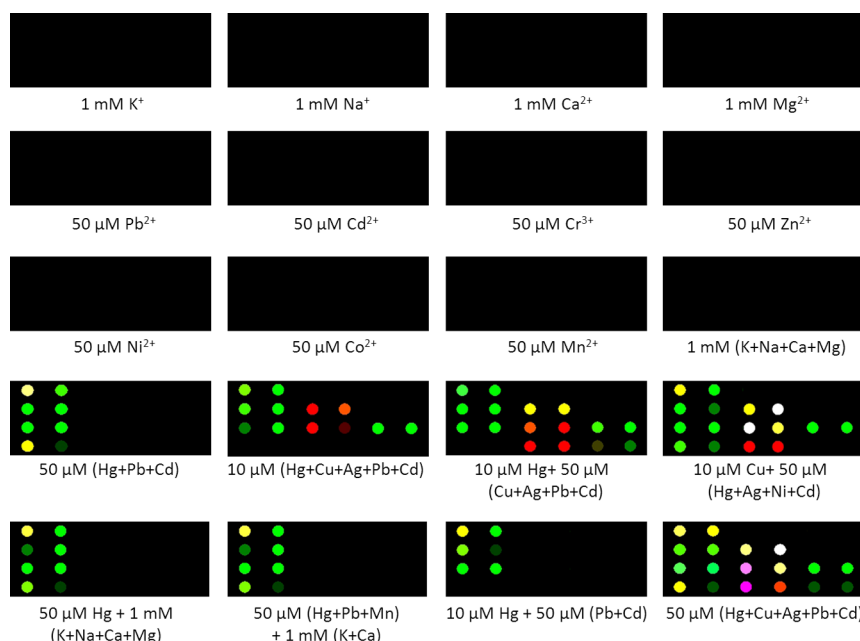


Figure 6. Responses of the developed test strip to the 11 common metal ions and to Hg^{2+} , Ag^+ , and Cu^{2+} with the presence of these metal ions. For display purposes, the color range is expanded from 2 to 8 bits per color (RGB range of 2–5 expanded to 0–255).

Anti-Interference Capability. Good anti-interference performance is another critical issue which should be considered when using a test strip in the “real-world”. Since our test strip is fabricated by specifically responsive indicators, it would not respond to other common metal ions. As expected, none of the following common metal ions, e.g., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+} induce noticeable responses to the array test strip (Figure 6). It is important that highly analogous response patterns are observed in the presence and absence of several other metal ions coexisted in the sample solution for detection of Hg^{2+} , Ag^+ , and Cu^{2+} (Figure 6). These results indicate excellent anti-interference capability of the developed colorimetric array test strip.

Applicability for Real Water Samples. The real wastewater samples were used to evaluate the potential of the developed test strip for Hg^{2+} , Ag^+ , and Cu^{2+} . Two real water samples were simply collected from the lab’s tap and the pond in our institute. As shown in Supporting Information Figure S5, the test strip exhibits analogous responses to Hg^{2+} , Ag^+ , and Cu^{2+} whether they are in deionized water or in real water samples (i.e., tap water and pond water) at various concentrations. These findings demonstrate that the as-fabricated colorimetric array test strip can be potentially applied in real wastewater samples.

CONCLUSIONS

In summary, we have developed a simple approach to fabricate a colorimetric array test strip for both qualitative and semiquantitative multianalyte analysis. The basic idea of this approach is embedding specifically responsive indicators in appropriate matrixes and achieving tunable sensitivities. As a proof-of-concept application, a multi-ion analysis array test strip (for Hg^{2+} , Ag^+ , and Cu^{2+}) was fabricated in this study. The as-obtained test strip shows not only highly selectivity of Hg^{2+} , Ag^+ , and Cu^{2+} , respectively, but can be applied for their mixtures (even in the presence of other metal ions). The

calculated sensitivities (LOD) of the test strip for Hg^{2+} , Ag^+ , and Cu^{2+} are well below the Chinese wastewater discharge standard concentrations. Moreover, this array test strip shows good anti-interference capability, detection, and production reproducibility, long-term storage stability, and real water sample applicability. Compared with the traditional colorimetric sensor arrays, our approach would be applied for fast recognition and discrimination of multiple analytes (e.g., Hg^{2+} , Ag^+ , and Cu^{2+}) simultaneously in both qualitative and semiquantitative manners without requiring complex statistical analysis.

ASSOCIATED CONTENT

Supporting Information

Formulations for immobilization of indicators, array’s time-dependent responses, detection reproducibility, production reproducibility, storage stability, and real water samples applicability of the colorimetric array test strip to Hg^{2+} , Ag^+ , and Cu^{2+} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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